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PATENT SPECIFICATION

DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process and Apparatus for the Production of Bituminous Coverings of Fine Sand (known as Slurry Seals)

We, ETABLISSEMENTS LASSAILLY & BICHEBOIS, 37 Boulevard Brune, Paris (Seine), France, and SOCIETE DE PRODUITS CHIMIQUES D'AUBY, 46 Rue Jacques Dulud, Neuilly-sur-Seine (Seine), France, both French Joint Stock Companies, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process and apparatus for the production of bituminous coverings of fine sand (known as slurry seals) which are used especially for covering road surfaces and which are produced with cationic emulsions.

Anionic slurry seals are known and used. It has been proposed to use cationic slurry seals which are better than anionic slurry seals, especially because there is better envelopment of the fine sand and adherence, and also better resistance against wear by weathering. Cationic slurry seals have the further advantage that a road covering produced with them can be put into use sooner, thanks to the comparatively rapid breaking up of the cationic emulsion used.

Cationic slurry seals have not become widely used because in most cases the powerful attraction between the cationic emulsion and the very large surface formed by the fine and more or less positively charged sand particles causes premature, almost immediate, breaking up of the cationic emulsion, which makes the use of these slurry seals under practical conditions difficult.

It is an object of this invention to overcome as far as possible this difficulty.

According to this invention in a process for the production of a bituminous cationic covering of fine sand particles, mixing is carried out in two immediately successive phases, in the first phase an isolating substance being added to a mass of particles, such that they are temporarily isolated physically and (or ionically, and in the second phase a cationic treatment emulsion being added to the mass such that the temporarily isolated particles are enveloped by the emulsion. Preferably the process is carried out in a single mixing apparatus.

Breaking up of the emulsion is therefore not a disadvantage; it may even be retarded if this is considered to be advantageous, according to the conditions under which the material is to be used (for example the type of sand and its moisture content) in order to be able to control the time before which the slurry seal can be used, or if desired in order to be able to use it without delay, and the main qualities of cationic slurry seals compared with those of the other slurry seals are maintained or even improved.

Isolating substances that may be used in the first phase are numerous and may be either non-ionic and/or cationic.

They are advantageously from the family of amines and more particularly from the following compounds:

A. Salts of amines or polyamines and an organic or inorganic acid, in which the general formula of the amine or polyamine is:

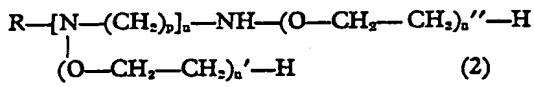
$$R—[NH—(CH_2)_b]_n—NH_2 \qquad (1)$$

wherein R designates a radical of an aliphatic or cycloaliphatic hydrocarbon, saturated or unsaturated, of the straight-chain or branched-chain type, which comprises 8 to 22 and preferably 14 to 18 carbon atoms, n is an integer selected from 1 to 8 and pre-

[*Price 4s. 6d.*]

ferably from 2 to 5, and p is an integer selected from 2 to 6, preferably 2 or 3. These compounds exert an adhesive effect by cationic adsorption on the surface of the materials to be coated. They also have a foaming and surface-tension reducing power.

B.—Nitrogen-containing compounds having the following general formula:



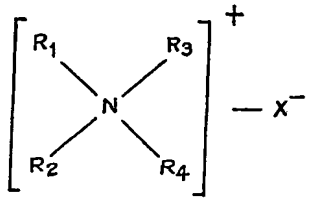
(2)

wherein R, n and p have the same meaning as in formula (1), and n' or n'' is an integer of from 5 to 15 according to the desired water solubility.

These compounds may be obtained by fixation of the oxyethylene or oxypropylene groups on the alkyl-polyalkylene-polyamines.

These compounds have foaming power as well as surface-tension reducing power. They also promote adhesiveness to assist in forming an ionic protective barrier.

C.—The quaternary ammonium salts according to the conventional general formula:



(3)

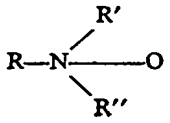
that is, consisting of substitution derivatives on the functional nitrogen of hydrocarbon radicals of which at least one has a linear or branched chain comprising from 8 to 22, and preferably from 14 to 18, carbon atoms.

These products exert a surface-tension reducing action and also a foaming effect. Furthermore, due to their adhesiveness they build up an ionic protective barrier.

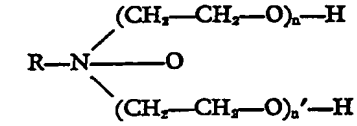
D.—Amine oxides and their derivatives according to the following denominations and formulae:

(a) Alkyl-dimethylamine oxide (4)
Alkyl-diethylamine oxide
Alkyl-dipropylamine oxide

(b) Alkyl*poly*hydroxyethylamine oxide, and more particularly alkyl*di*hydroxy-*ethyl*amine oxide (5)
or alkyl-polyhydroxypropylamine oxide



(4)



(5)

wherein R designates an aliphatic or cycloaliphatic radical, saturated or unsaturated, having a straight or branched chain, with from 8 to 22 and preferably from 10 to 14 carbon atoms; R, R' and R'' are aliphatic radicals comprising from 1 to 3 carbon atoms; n and n' are integers from 2 to 16 and preferably from 2 to 4.

These amine oxides have a foaming, foam-regulating and stabilizing power. These properties are well known and used in other, very different applications. They do not interfere whatsoever with the adhesivness of the binder on the inorganic particles since they are moderately polar, water-soluble and thus eliminated with water when the emulsion breaking phase takes place. Moreover, they permit of producing more concentrated A, B and C mixtures for a same viscosity of their aqueous solution. These aminated oxides are obtained from tertiary amines treated as already known with hydrogenperoxide, ozone or other oxidants.

The products set forth in paragraphs A, B, C and D above may be used either separately or in mixtures of two or more, or even mixed with complementary products in variable proportions according to the nature and granulometry of the materials involved.

The pH value of the aqueous solution of these A, B, C and D products or mixtures thereof also depends on the specific materials utilized. As a rule, this pH value lies within the range of from 1.5 to 6 and preferably between 1.5 to 4, which is quite satisfactory in most cases occurring under practical conditions for stony materials having a sand equivalent of at least 30.

In a laboratory experiment (Example No. 1) constituting an application of the method of this invention 100 grams of dry fine sand have been treated, this sand having a siliceous nature and having the following characteristics:

sand equivalent = 30
fillers = 15%
granulometry = up to 5mm. (particle size)

The sand was treated with a dispersion, in 10 grams of water, of amine oxide obtained from alkyldimethylamine, the alkyl radical is preferably the same as that in coconut oil.

It was observed that the fine sand was transformed into a temporary state of pseudo-thixotropic suspension, this transformation being sufficient and lasting a sufficient time to permit the application of a treatment with the assistance of a conventional cationic bituminous emulsion and produce a valuable bituminous slurry seal. In this example (Example 1) the slurry set after about 10 minutes.

In another example (Example 2) a specially dispersible and sufficiently emulsifiable coating polyamine was used in autumn in France, for treating under relatively favourable hygrometric conditions at a temperature of about 12°C (54° F) 10 tons of rolled and washed sand having a granulometry summarized in the following Table:

Sieve mesh size millimeters	Percentage of passing material
5	100
2.5	82
1.25	66
0.63	40
0.315	28
0.16	18
0.08	7

This sand was extracted from a mainly siliceous sand-pit.

This sand was treated with 1,000 litres of water in which 11 kg. of a tripropylene-tetramine (therefore soluble) with C=18, n=3 and p=4, had been poured. This polyamine had been obtained from a commercial fatty acid having substantially the following composition:

stearic acid	:	42 %
lauric acid	:	2.5%
myristic acid	:	1.5%
palmitic acid	:	51 %
palmito-oleic acid	:	3 %

The binder was a cationic bituminous emulsion obtained according to a conventional method and having the following formula:—

—To three kilograms of a polyamine mixture of which the main constituent was a tripropylene-tetramine wherein C=18, n=3 and p=4, there were added 4 kg. of hydrochloric acid at 22° Bé, these ingredients being dissolved in 400 litres of water at 70°C. Then 600 kg. of bitumen having a 180/220 or 80/100 penetration were weighed and heated to 120°C. This bitumen was emulsified in the said solution using a mixer of the colloidal mill type. The resulting emulsion had amongst other characteristics a cold viscosity as usually demanded from bitumen emulsions. The time necessary for carrying out the method of this invention did not exceed about 20 minutes. Thus, this invention makes it possible to produce a bituminous slurry seal having the advantageous features set forth above. This bituminous slurry seal spread directly on a damaged road surface provided a quality road surface coating which it could be used under normal traffic conditions after only 40 minutes.

In another example, the two formulae of Examples 1 and 2 were combined with a view to commercial preparation of a cationic bituminous slurry seal for road application.

In this Example (No. 3) 10 tons of fine sand having the same granulometry as set forth above with a 7% water content were treated just before mixing the sand with the cationic emulsion, by using in 200 litres of water a dispersion of:

(1) 5.6 kilograms of a polyamine (coating) mixture to which HCl has been added up to a pH value of 2.5;

(2) 1.6 kilograms of an amine oxide (foaming and of adequate stability) as in Example 2.

The proportion of foaming agent in relation to the coating agent was thus 28%. As a rule, this proportion may range from 5 to 40%, and preferably from 20 to 30%.

The cationic bituminous emulsion used had the following composition:

80/100 bitumen:	60 kg.
Water:	35.5 kg.
Hydrochloride of fatty polyamine+HCl up to pH=3	4.5 kg.

1,500 kilograms of this emulsion were used to coat the 10 tons of fine sand.

Under these conditions a bituminous slurry seal of exceptional quality, ready for normal service within less than one hour, was obtained. It was also observed that the efficiency of the process was maintained if the filler proportion in the fine sand was increased.

In other Examples (4 to 6) referring more particularly to the ternary mixtures of three classes of products A, B and C the "A" compounds consist of alkyloyl-propylene polyamines according to the general formula (1).

The substitution products for the "A" compounds may be those resulting from the acylation of polyethylene polyamines by means of higher fatty acids of which the chain linked to the functional group comprises from 14 to 18 carbon atoms.

Regarding the second group of compounds, namely those set forth above as "B" compounds, they are non-ionic compounds according to the formula (2) above.

Finally, regarding the last constituents of the aqueous mixture, namely compounds C, they are quaternary ammonium salts according to formula (3) above, preferably dodecyl-dimethyl-benzyl-ammonium chlorides.

It is particularly advantageous to salify, by means of an inorganic or organic acid, the organic compounds constituting the basis of the ternary aqueous mixture.

The salifying acid is preferably hydrochloric acid. However, other acids, for example acetic acid, may be used; likewise, A, B, and C compounds salified separately with different acids may be used.

The relative proportions of the three products A, B and C in the solution is also subordinate to the surface condition of the materials to be coated, or to their chemical composition. From the physical point of view, it depends on the other hand on the degree of division of the aggregate, that is, its granulometry, and in fact on its specific surface area.

The quantity of components A used in the ternary aqueous mixture increases as the affinity of the binder for stony material decreases, this being due to the fact that as already stated the adhesiveness of the "A" products is reinforced by a cationic adsorption of the amine function on the surface of the mineral to be coated. On the other hand, the cleaner and smoother the material, the smaller the required quantity of product C. Regarding the product B completing the ternary mixture, its quantity will depend on the specific actual surface area of the aggregate, which may be more or less smooth.

The total concentration of the A, B and C products in water may vary from 1 to 3%.

The aqueous solution of the ternary mixture of organic compounds A, B and C may contain from 1 to 5 kilograms of pure products per ton of fine stony materials to be coated.

In order better to illustrate the results obtained, there is described in the following Examples the coating of various types of sand of different origin but of a granulometry comparable to that given above (Example 2). In these examples, parts are by weight.

EXAMPLE 4

To coat a fine ground sand having a granulometry similar to that of the preceding examples, the sand is conditioned according to the method of this invention with an aqueous solution containing, for 150 parts of water, one part of product A, one part of product B and one part of product C.

The quantity of bituminous emulsion of the cationic type utilized for the coating operation proper is 150 parts by weight. The breaking time of the emulsion, which was determined according to the conventional methods, is 25 minutes.

The coating thus obtained is very satisfactory and has a good adhesivness.

EXAMPLE 5

To coat a fine sand similar to the preceding one but of different origin the sand is conditioned with an aqueous solution containing for 100 parts of water 0.5 part of product A, 0.5 part of product B and one part of product C.

The quantity of bituminous emulsion of the cationic type utilized for the coating operation proper is 150 parts. The breaking time of the emulsion, determined by resorting to the conventional methods, is 40 minutes.

The resulting coating is very satisfactory and has a good adhesiveness.

EXAMPLE 6

To coat another fine sand of similar granulometry, the sand is wetted according to this invention with an aqueous solution containing for 150 parts of water one part of product A, two parts of product B and 1.5 part of product C.

The quantity of bituminous emulsion of cationic type utilized for the coating operation proper is 150 parts. The breaking time of the emulsion, determined by means of the conventional methods, is 30 minutes.

The resulting coating is very good and has a good adhesiveness.

If the same tests as those described in Examples 4 and 6 are carried out but without using a pseudo-thixotropic wetting aqueous dispersion, of products A, B and C, it will be observed that in this case the coating cannot be effected.

The following Table gives comparative results to emphasize the considerable advantage resulting from the use of the wetting aqueous solutions or emulsions according to this invention in the last three Examples 4, 5 and 6 hereinabove.

Example	Coating without solution	Coating with solution	Breaking time in mn.
4	Impossible (immediate breaking)	very good	25
5	Impossible (immediate breaking)	very good	40
6	Impossible (immediate breaking)	very good	30

The method of this invention is advantageously carried out as applied more particularly to road surfacing structures by using a continuous equipment for the cold mixing

and spreading of a fine-granulometry bituminous slurry seal described hereinafter by way of example with reference to the single diagrammatic figure of the attached drawing showing a typical example of a mixing unit for producing this bituminous slurry seal, which is mounted on a truck 1 and intended for road surfacing works.

The fine sand aggregates are loaded into a hopper 2 delivering the sand for example by means of an endless belt conveyor 3 into a mixer 4 for example of the screw type.

The treated binder is delivered into the mixer 4 from a suitable source or reservoir 5 for the binder, which is provided with a metering device such as a cock or valve 6. The emulsion output is delivered substantially midway of the mixer screw.

According to the method of this invention, a source or reservoir 8 for delivering the aqueous solution or dispersion of the agent for the preliminary wetting of the aggregates delivers its contents at 9 in a zone where the aggregates are conditioned, between the end of the conveyor belt 3 and the point 10 of delivery of the emulsion into the screw 7. A control device 11 permits of regulating at will the output of the said dispersion for wetting the fine aggregates. Means may also be provided for metering the dispersion proper before its delivery.

The bituminous slurry seal mixture treated with the treated fine aggregates is delivered from the mixer 4 so as to be spread by means of a spray rack 12.

The surprising results obtained by using the method of this invention are attributed mainly not only to the characteristics of the additives used therein but also to the fact that the cooperation during the mixing step of the cationic bituminous emulsion and of the fine sands treated according to this invention creates a temporary ionic and physical isolation of the sand particles; this temporary state is such that breaking of the cationic bitumen emulsion is retarded during a time period sufficient to ensure setting of the bituminous slurry seal under satisfactory conditions, this setting being however sufficiently rapid to permit resumption of normal road traffic within a relatively short time.

The embodiments described above are not be construed as limiting and it would not constitute a departure from the invention to modify the nature and proportion of the constituents of the surface-tension agents cited by way of example; the mixtures of agents may also vary, particularly according to the nature of the aggregates available and to the conditions of application. The cationic agents used for the preliminary conditioning of the fine aggregates and of the bituminous emulsion may be the same, but they are preferably different, to permit better timing of the breaking of the emulsion according to the specific conditions of application. The cationic agents of the emulsion, in cases where practical conditions of application are relatively easy, may be of a less efficient but more economical character than those of the group cited by way of example.

Thus, the emulsion timing may be modified within the scope of this invention by introducing either adequate additives particularly adapted to reduce surface tension with respect to the action of atmospheric air, or products of which the surface-tension action with respect to air may be increased by virtue of the action of physical or mechanical means, or otherwise. The mechanical stirring action in the example described assists in producing the results set forth.

In the apparatus used, which may be of very different types, the character, number, arrangement and assembly of the component elements may vary according to the specific applications contemplated, the requirements and circumstances. For instance, provision may be made, for a plurality of successive sources or reservoirs such as 8, for successively introducing along the mixing process the additives intended to produce the complementary effects. In fact, it is obvious that even if some of the polyamines according to the invention may frequently prove sufficient when used alone, due to the polyvalence of their essential effects, these effects may however be increased or improved by the presence in the preliminary dispersion, and also in the final emulsion, of other additives having adequate complementary inherent characteristics of which the action will not impair the favorable effects of the cationic agents and more particularly those of the amine or amines or polyamines used in accordance with this invention, or their derivatives.

For example if ground aggregates are used two containers (or a greater number of these, if desired) may be filled respectively with fine sand and very fine sand (filler), only one of the two types of fine sand (the one more suited for undergoing a conditioning treatment) being subjected to the preliminary cationic treatment. The method and the equipment according to this invention may also be used for the preliminary conditioning of fine sands used as component element in aggregates having a granulometry corresponding to the preparation of bituminous coatings, i.e. aggregates of a so-called standard granulometry type. The method and the simplified equipment according to this invention may further be used for coating and spreading complex sands treated beforehand by known means with a view to making them insensitive on the one hand to the action of water and on the other hand to the segregation of their various constituents. It should also be understood that although the best results have been obtained by using apparatus as described

above, which permits of obtaining in the mixer the desired temporary isolating thixotropic state, the method of this invention may admit in some cases some time lag between the wetting of the fine sand and the mixing thereof with the treated binder, but this time period must be limited, otherwise the desired results will not be obtained completely.

WHAT WE CLAIM IS:—

1. Process for production of a bituminous cationic covering of fine sand particles wherein mixing is carried out in two immediately successive phases, in the first phase an isolating substance being added to a mass of particles, such that they are temporarily isolated physically and/or ionically, and in the second phase a cationic treatment emulsion being added to the mass such that the temporarily isolated particles are enveloped by the emulsion.

2. Process according to claim 1 wherein the isolating substance is also a foaming agent for producing an expanding effect on the mass.

3. Process according to claim 1, wherein the isolating substance is selected from polyamines or derivatives thereof which correspond to the general formula:—

$$R—NH—(CH_2)\ P_n—NH_2$$

in which R is an aliphatic or cycloaliphatic, saturated or unsaturated hydrocarbon compound having a straight or branched chain which has from 8 to 22 carbon atoms, or the corresponding acyclic material in which the oxygen atom is held by the carbon atom that is linked to nitrogen, and n is from 1 to 8 and p is from 2 to 6.

4. A process according to claim 3 wherein the straight or branched chain has from 14 to 18 carbon atoms.

5. A process according to claim 3 wherein n is from 2 to 5.

6. A process according to claim 3 wherein p is 2 or 3.

7. A process according to any preceding claim wherein the isolating substance is an amino-oxide.

8. A process according to any preceding claim when carried out in mixing apparatus having a mixing container, a first inlet in the container for entry of the cationic emulsion, and a second inlet in the container for the isolating substance, the second inlet being above the first.

9. Processes for the production of cationic slurry seals substantially as herein described.

WITHERS & SPOONER,
Chartered Patent Agents,
148—150, Holborn,
London, E.C.1,
Agents for the Applicants.

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1,109,893 COMPLETE SPECIFICATION

1 SHEET

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